Environment Engineering: Chemical Processes

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Module No # 06
Lecture No # 28
Alkalinity: Introduction

Hello everyone so welcome back to our latest lecture session so I believe in the last session we have been talking about discussing titration and buffers. So buffer is one we would look at let us say when you want to resist the change in PH when the acid or base is added and we looked into relevant example so I believe what is it now the monprotic acid which I think we looked at with relevant acetic acid and then we diprotic acid which in that case we looked at carbonate system.

So at the carbonic acid and the relevant acid base species so again we are now going to come back to design in buffers I believe we briefly discuss this earlier but we are going to see or you know briefly summarize what we are up to right.

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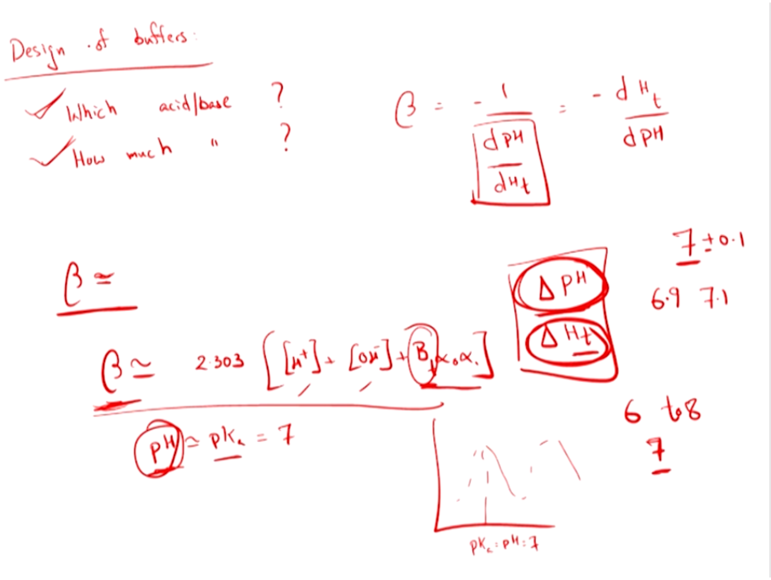

So design of buffers so when you are trying to design a buffer what is this mean when you want to choose the relevant acid base system or the species right and you also want to know how much acid or the base you need to put into your system right so what are we trying to look at which particular acid base to add right and also how much of the acid base you want to add?

So how do you come up with this now right? So for this obviously you need to able to look at what it is you need as in what PH change are you comfortable with so only then you can able to come up with the relevant buffer intensity so we know that buffer intensity what was that equal to -1 / derivative of PH into H total right and that was equal to –DH total / DPH or let me just use this variable I guess.

So let us say you know let us say what is the change in PH or delta PH change you are fine with to the change in total let us say this you can know right are you fine with the change in PH if you are trying to buffer a system with PH7 and you want to or you only fine with 6.9 to 7.1 let us say + or 1 7.1 you know you will have the particular buffer intensity and let us say if you okay with 6 to 8 right when your PH is you want to PH is estimating at I want to buffer this system is at 7 right then you have a lesser buffer intensity so that is what you see here.

And you need to obviously estimate H total as has not estimate the total acid or base that you think will be added to the system so once you can understand how much PH change you are okay with and you know how much acid or base will be formed in the system during the experiment or in the natural system then you can obviously come up with calculating the buffer intensity approximately right.

So you have the buffer intensity now so you know how much not how much buffer intensity and what is that equal to you know that is equal to 2.303 into concentration of H+ + OH- + let us say for the monprotic acid what is it now B total alpha naught into alpha1 right so for a specific PH let us say you know you have H+ and OH- to be you can calculate that right they are fixed so you need to be now be able to calculate how much B total you need for that obviously you need to choose how much acid.

So how are going to choose that you are going to choose as the PH will be equal to the PKA of the system and which you in this case we want to be 7 so you can look at the relevant acid and base that are available and then you can see which particular you know PKA will be relevant to PH 7 right and which case we have PKA = PH 7 so you might not have something that is or you know not find a system that would you know play a passive role in experiment and all also you know be equal to nearer the PH of 7.

So you need to go with some you need to have some levy here the carbonic system or carbonate acid you know that it is a PKA1 of 6.3 and you are trying to buffer it 6.7 okay you can live with that you can choose that or the phosphoric acid it has 3 PKA values what is it what are they around 2.3, 6.7 or 7 and 10.3 so that something you can choose phosphoric acid right.

So again so what do you need so once you calculate the buffer intensity you need to choose which buffer or which compound to choose so how are going to go with that you are going to choose a compound whose PKA is near the PH you are trying to buffer it right so once you get that you obviously have which acid base to choose right and how much you can calculate the total from the buffer intensity or the this equation and done with the 2 variables so that is the design again.

First you need to look at how much PH change with or live with and then you are going to calculate obviously what now the buffer and then from that you will choose the relevant buffer which particular system you want to choose so for example of PH7 we said carbonic acid or what is it now the phosphoric acid with the PKA around 6.3 and 6.7 respectively right and then once you have that you can plug that in and get the total base or total acid that you need to add right.

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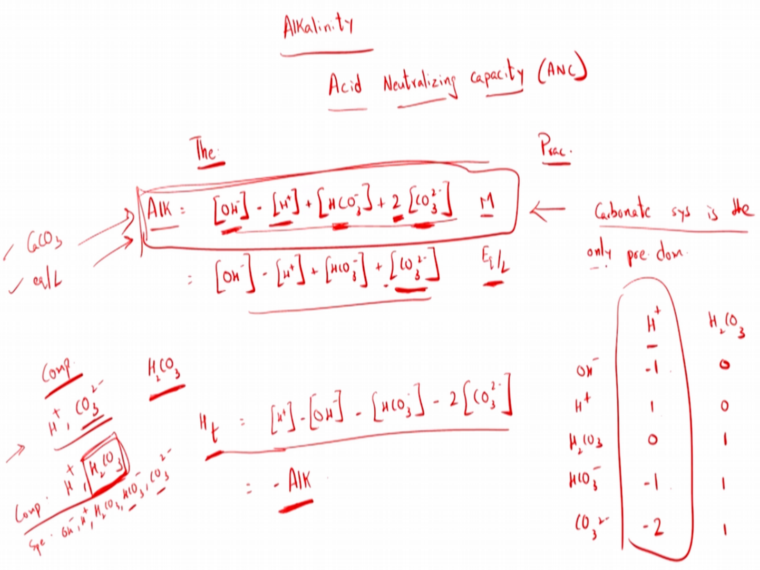

Alkalinity

Acid Neutralizing capacity (ANC)

The. Prac.

$$\mathrm{Alk} = [OH^-] - [H^+] + [HCO_3^-] + 2[CO_3^{2-}] \quad M$$

$$= [OH^-] - [H^+] + [HCO_3^-] + [CO_3^{2-}] \quad Eq/L$$

✓ $CaCO_3$

✓ eq/L

Carbonate sys is the only pre. dom.

Comp. H^+, CO_3^{2-}

H_2CO_3

Comp: $H^+, \boxed{H_2CO_3}$

Spe: $OH^-, H^+, H_2CO_3, HCO_3^-, CO_3^{2-}$

$$H_t = [H^+] - [OH^-] - [HCO_3^-] - 2[CO_3^{2-}]$$

$$= -\mathrm{Alk}$$

	H^+	H_2CO_3
OH^-	-1	0
H^+	1	0
H_2CO_3	0	1
HCO_3^-	-1	1
CO_3^{2-}	-2	1

So with that we are going to move on so now we are now going to discuss Alkalinity right and that is something that is our present in all the natural system so that is of considerable importance to environmental engineers but before we go further let us look at why we need to look at alkalinity I guess right. So in of the previous example or session that we looked at I believe we considered an open system where we can carbon dioxide in the gaseous phase and which is need to equilibrium with your aqueous phase right.

And then we knew that we now know that you know carbon dioxide if it what do we say changes in phase from gaseous to aqueous phase it can form H2CO3 in your aqueous phase and then we are going to end up with an acid in your particular system and then the relevant dissociation into either HCO3 – or HCO32- yes but in effect let us say we are going to have an acid what do we say added to your particular aqueous system so in general let us say you know that the PH can go down so let us say how would you arrest this particular decrease in PH in natural system right.

So in that case alkalinity comes into play make sense so again alkalinity would help our system looking at neutralizing the acid so you would also called acid neutralizing capacity. So let us look at what we are up to here so we are now going to discuss alkalinity so at we can also understand at why the acid neutralizing capacity yes and you know the important aspect is our presence right.

You know because you have carbon dioxide and source of CSCO3 and in your C beds right you are always going to have considerable alternative in your particular system natural system pardon me and so thus that pardon me variable that you always need to consider obviously depending on the relevant organic or inorganic reactions or the interaction with these particular component right.

So again this is our presence and that is the reason we are going to look at it and one particular aspect with help us in our natural systems is that it pressure the change in not change pardon me decrease in PH buffer would resist the change in PH in either direction as in either decrease or increase with addition of acid or base right but here we are talking about resisting decrease in PH whenever there is addition of your acid right.

So here we are going to move on to that so here we are going to look at two aspect once the theatrical definition and once would be the practical definition which are practical measurement which we look at in the lab and so alkalinity it is define as the concentration of OH- - concentration of H+ + concentration of HCO3- + two times the concentration of HCO32-. SO obviously this would be when the case are in unit or molar units but if they are equivalence in per liter or equivalence let us say the units what are they going to be OH - - H+ + HCO3 - + CO32- right.

So again the difference here is that in the in this case we are using the molar units and here we are using the equivalent here right or the equivalence here so alternative can be expressed in terms here either CSCO3 or equivalence per liter usually these are the two what do we say been looked at to alternative now. So again now let us try to understand what it is that we are looking at here let us look at each of the component in general we are going to look at this particular equation now right.

So it is acid neutralizing capacity so more or less fine to look at or quantify all the basis we are going to be present in your system. So OH- HCO3 and CO32- because CO32- when take or neutralize to protons that is why are have a two terms here and obviously if we look at the equivalence or do not we need to have this here because that will be taking care or when you calculate the equal concentration here again so we need to look at all the basis present in system they are OH- HCO3 – and CO32 – twice 2 because it can neutralize 2 protons right and obviously you need to subtract the protons here.

And this obviously would be valid again what now in carbonate system is the only predominating is the only predominant acid base system in your particular solution right. So again the theatrical definition consider that only the carbonate system is the predominating acid base system between your particular solution here and based on that alternative nothing else but acid neutralizing capacity right.

So if you putting in acid or you know titrating your solution with an acid let us say right what are the compounds would neutralize your particular acid and so we list the relevant basis here which is OH- right always present in solution and then HCO3 – and CO32- which the relevant coefficient and obviously subtract H- right and again this is a working that most people understand but let us look at the fundamental of the basis for this particular aspect right.

So in general if you look at this particular case and this you can believe look at stem and morgan in this particular case. So in general if we look at particular balance right if we remember we always looked at them with respect to H+ and the most deprotonated form CO32- but in this case let us say if we consider the reference to be H2CO3 right so the alkalinity titration with respect to going to be respect to the reference of H2CO3 now.

So in that case instead of having CO32- if we consider of components to be H+ and H2CO3 right what would H total be let us try to write that and what are our species here and other new components that I am considering are H+ and H2CO3 and what are the species OH- H+ and what else H2CO3 HCO3 – and CO32- and thus obviously is in the close system right.

So H total is going to be equal to what now H+ obviously right and what else – OH- yes and now because we have components has H2CO3 and now CO32- so you are going to have two what do we say terms here so addition terms here and what are they HCO3 - - two times of CO32- right again if people are unable to understand this let me plug this off here or plug this down here we have H and what do we have here H2CO3 this is nothing but tableau right and these are the various species OH- H+ and H2CO3 let me write that down I guess HCO3- and CO32-.

So how many H+ do I need to form 1 OH- -1 and this is going to be 0 and how many H do I need to form OH+ 1 and this here going to be I need 0H2CO3 to form H+ and again here it is going to be 0 and 1. And obviously HCO3- is H2CO2 – H+ so that is why we have it here and how can I form CO32- by H2CO3 – two times of H+ and from this we can look at the total component balance which is H+ - OH- HCO3 - - CO32- and this is nothing but as you see – the activity here right.

So in effect the total H you know it is going to be negative of the alkalinity the theoretical definition of alkalinity especially when you consider your reference or the components to be your H2CO3. So again the reason we are going at will be aprint later but please keep this mind that where the reference is with respect to the component H2CO3 right again the theoretical definition is valid when only the carbonate system is the predominating system.

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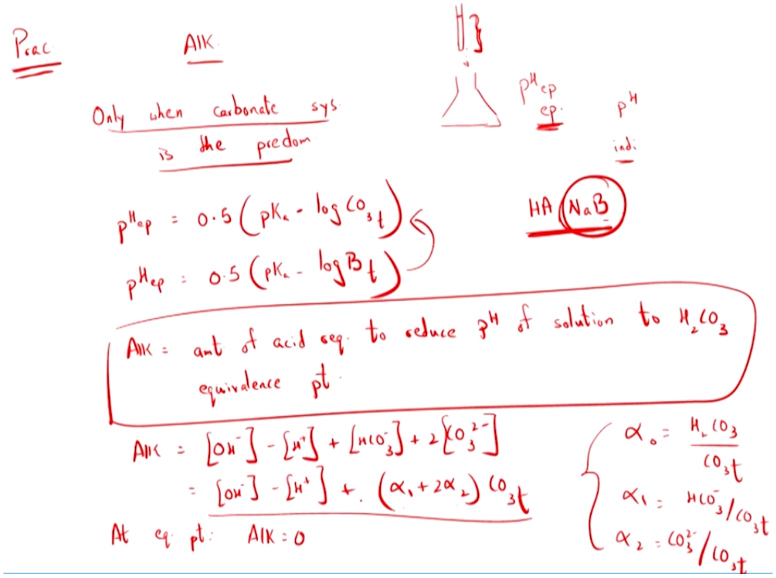

Prac

Alk

Only when carbonate sys is the predom

pH_{ep}

ep

pH

indi

$\mathrm{pH}_{ep} = 0.5\left(pK_a - \log CO_{3t}\right)$

$\mathrm{pH}_{ep} = 0.5\left(pK_a - \log B_t\right)$

HA NaB

Alk = amt of acid req. to reduce pH of solution to H_2CO_3 equivalence pt.

$\mathrm{Alk} = [OH^-] - [H^+] + [HCO_3^-] + 2[CO_3^{2-}]$

$= [OH^-] - [H^+] + (\alpha_1 + 2\alpha_2)\,CO_{3t}$

At eq. pt: Alk = 0

$\alpha_0 = \frac{H_2CO_3}{CO_{3t}}$

$\alpha_1 = HCO_3^- / CO_{3t}$

$\alpha_2 = CO_3^{2-} / CO_{3t}$

So let us go back to the practical definition here right and how do you know about measuring your particular alkalinity right and the lab. So in general I guess lab what do we say the initial here right and then you have you are going titrate it with strong acid yes and then you end up measuring particular color change or end point.

So the key here is you have an end point right you end up measuring the amount of acid that is been consumed to reach that particular end point which is either measured by you know you can use your PH meter or you know depending upon the indicator that you want to look at right which you would give a color change in that particular PH 10 point yes this is how we are going about it.

So here in general let us say when would the practical definition of your alkalinity or practical measurement of alkalinity be the same as what you would calculate from your theoretical definition again when is that only when the carbonate system is the predominating system right yes. So again the end point we typically look at something that we can calculate.

So I believe we looked at that we are buffer intensity and such when we are trying calculate the equivalent point what was that I think PH of the equivalence point to a 0.5 times PKA – log CO3 total right and this is something that we end up with or ended up deriving when we considered system where we had the strong acid HA and a week acid NAB right and CO3 total is for NAB yes and this is something that we calculated there I mean we calculated something like PH = equivalent points = 0.5 times PKA – log B total right.

But obviously in this case you are POC3 and that is why we end up with equation but you might be you know this people who are paying closer attention right might be able to point out that in this particular derivation here we looked at let us say only monoprotic week acid right. But here your carbonate system here H2Co3 is diprotic acid so you know let us see you know but it turns out that you know looking at relevant underlying acid that relevant equation is still valid but let us see how we can go about that.

So again what is the experimental definition here alkalinity would be equal to the amount of acid required to reduce PH of solution to and what was our reference earlier remember that close the H2CO3 equivalence point this is the practical definition I guess right and we looked at the theoretical definition earlier yes and so now how do we go about this how do we you know end up calculating end up points here right.

So we did look at one particular case by again as I just mentioned you know it is for mono protic what do we say week acid right tight against a strong acid and we end up calculating the equivalence point then right and so here let us see how we can go about it here keep in mind that here we are measuring the acid neutralizing capacity right. So we are adding enough acid to be able to neutralize this particular take care of this particular acid capacity.

So at that equivalence point the key is that the activity is going to be 0 why is that because you add enough acid to be able to such that A is that alkalinity so that is what particular equation or where does that leave it was so the alkalinity which is equal to what now the concentration of OH- - H+ + HCO3 - + 2 times of CO3- right and what we have and let me try to simply this further so that is going to be OH- -H+ + alpha 1 – 2 alpha 2 into CO3 total again to refresh your memory what do we have what are these alpha 1 and alpha 2 ionization factors.

So alpha naught will give an idea about H2CO3 / CO3 total whereas alpha 1 and alpha 2 would give an idea about there species which are deprotonated here HCO3 – by CO3 total and CO2 total / CO3 total. So looking at this particular or these particular variables that we are aware of earlier you know we end up with particular equation but we know that at equivalence point what do we know? The alternative is equal to 0 so let us mug this in here please.

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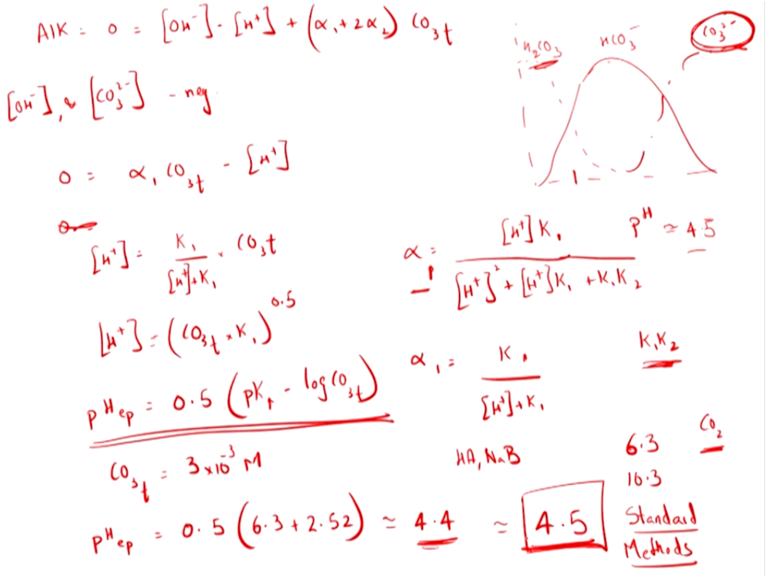

$Alk = 0 = [OH^-] - [H^+] + (\alpha_1 + 2\alpha_2)\,CO_{3t}$

$[OH^-], [CO_3^{2-}]$ - neg

$0 = \alpha_1 CO_{3t} - [H^+]$

$[H^+] = \frac{K_1}{[H^+] + K_1} \cdot CO_3t$

$[H^+] = (CO_{3t} \times K_1)^{0.5}$

$pH_{ep} = 0.5\,(pK_1 - \log CO_{3t})$

$CO_{3t} = 3 \times 10^{-3}\ M$

$pH_{ep} = 0.5\,(6.3 + 2.52) \simeq 4.4 \simeq \boxed{4.5}$

$\alpha = \frac{[H^+]K_1}{[H^+]^2 + [H^+]K_1 + K_1K_2}$

$pH \simeq 4.5$

$\alpha_1 = \frac{K_1}{[H^+] + K_1}$

K_1K_2

HA, NaB

6.3

16.3

CO_2

Standard Methods

So the alkalinity = 0 = what now OH- - H+ + alpha right + alpha 1 + 2 alpha 2 times CO3 total and we know that you know from our carbonate system what is that let us say and this is our PH here. This is the speciation diagram here we are looking at right so H2CO3 this is the profile HCO3 this is the profile and for a CO32- this is the profile here.

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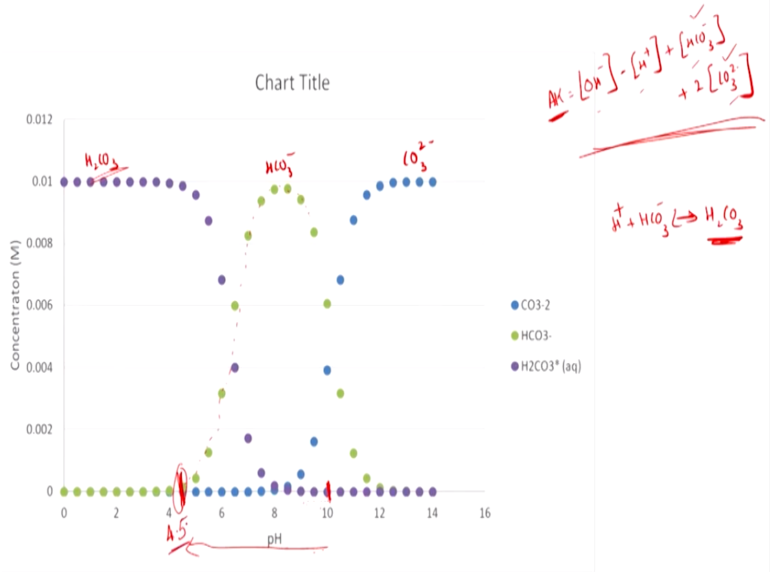

$Alk = [OH^-] - [H^+] + [HCO_3^-] + 2[CO_3^{2-}]$

$H^+ + HCO_3^- \rightleftarrows H_2CO_3$

I believe I have figure here right this is what we also looked at with respect to buffering density and such right so this is H2CO3 here. HCO3- here and CO32- right. So at which particular point do you end up let us look at this try to approximate the scenario end up neutralizing all the basis present and that too with respect to H2CO3 so the basis or CO32- and HCO3- so if it this particular point we now have not neutralize anything here.

And even at this particular point or you know point at this particular PH of it we still have HCO3- so we further need to try to it all the way to bear around 4.5 right where you would end up let us say neutralizing al the basis which are CO32- and HCO3- in your particular system keep in mind that the reference is H2CO3 here right so it is approximately it is 4.5 that is what around stand methods uses so we are going to come back to that and here we have CO32- right.

So again what are you trying to point out was that at that particular PH you know which was around 4.5 let us go back to figure the better place right you see that CO32- is negligible you know HCO3- would be at very low quantities but CO3 – is certainly remarkable in general right so that is keep that in account. So also it is 4.5 to PH the OH – concentration is also negligible so neglecting OH- concentration and what else the CO32- concentration right we are going to try to simplify this further so = alpha 1 times CO3 total – concentration of H+ and what is alpha 1 here.

Alpha we know it is going to be in this case let me try to write alpha naught in this case the dominator will be equal to H+ square what now H+ into K1 + K1K2 the equilibrium constants so now if we write down the denominator and now be sure of being able to write down the alpha 1 that is going to be equal to H+ into K1 right if it is alpha naught it would have been H+ square by this denominator alpha 1 by this particular term H+ into K1 by the denominator and alpha 1 into K1K2 / this particular term in the denominator right again.

So at this particular case let us see how we can you know simplify this further s alpha 1 let us say trying to simply with this further and that I can write as K1/ H+ +K1 and why is that because K1, K2 will be let us say negligible when H+ concentration is higher and once assign for that I can cancel out H+ so K1K2 will be negligible when H+ concentration is high which is the case because PH = or around 4.5 right.

So I am neglecting K1 and K2 in this particular term in the denominator so then I can calculate in H+ and then I end up with K1/ H++ K1 and so 0 = or let us say H+ = what now alpha one is K1 / H++ K1 into CO3 total right. And so if I end up solving for that H+ will be equal to CO3 total into K1 to the power of 0.5 and now we get this relevant similar form right so PH of the equivalent point it nothing but 0.5 PKA – or PKA or PKA1 in this case right – log CO3 total and as you see this similar to our particular case when we looked at the list HA and NAB and why is that?

Because at PH of 4.5 right we are neglecting CO32 – so in effect this system we are considering that to be a monoprotic system here. So we have so we end up with this particular equation so let us plug in the particular set of values I think I have an example here is that CO3 total if I take that to be 3 into 10 power -3 molar right and what is the PH at the equivalence point PH 0.5 times PKA 1 we know it 6.3 and PKA 2 is around 10.3 so that is what we are going to use here 6.3 – log of 3 into10 power -3 of the value I have here is 2.52 right.

So now I end up with something around 4.4 right and I end with around 4.4 and this as you see is remarkably or you know similar or nearer to the method of PH pardon me that is going to be followed by the standard method right. So the standard method would define your particular alkalinity as titrant with acid and until you reach the equivalent point of H_2CO_3 and to account for loss of CO_2 into the system into not the system into the gaseous phase during the titration and such standard method would more or less specify or not more or less pardon me would specify and N point of 4.5 right.

So again we just looked at relevant derivation with respect to alkalinity so let us look at what that means right let us say initially now my particular system is around PH 10 let us say right so I can calculate given the CO3 right I can calculate what alkalinity is going to be equal to and we know that from particular cases of our definition of alkalinity OH- - H+ +CO3 - + 2 times of CO32 – are present here right this is the theoretical definition.

So again practically what happens now let us say I am starting at PH10 and I want to end up with 4.5 so that means you know I need to obviously add an acid or titrated with an acid so I am starting from 10 and keep adding acid what is going to be consume here H+ is going to consume by HC03 – right any H+ is going to add is going to be initially neutralize by HCO3- and we transform into H_2CO_3 keep in mind that H_2CO_3 was reference right.

So keep going down and as you see HCO3- the concentration that keeps changing decreasing so on until almost all of it but not all of it though is going to be in the form H2CO3 but not all of it though is going to be in the form of H2CO3 and that is you understand in your particular system too right so these are the concentration at PH particular 10 you can calculate the relevant concentration and you can plug them in or obviously you can also titrate that and then calculate that.

But because you know how to use VMINTEQ for such you can calculate the equilibrium concentration of HCO3 – CO32- from VMINTEQ and plug them in or you can go back to the lab and titrate and look at amount of acid required to be able to neutralize the particular solution or neutralize pardon me reduce the PH of the particular solution to H2CO3 equivalence point which is 4.5 right.

So with that I will end today’s session and then in tomorrow session or pardon me the next lecture session we are going to look at let us say when would your particular practical definition of alkalinity and not the similar or you know not been considered with your theoretical definition of alkalinity and depending on time we are also going to start talking about acidity which is nothing but let us say base neutralizing capacity I guess right and with that I will end today’s session and thank you.